ELECTROCHEMICAL CONTROL OF IODINE DISINFECTANT FOR SPACE TRANSPORTATION SYSTEM AND SPACE STATION POTABLE WATER

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ABSTRACT

The National Aeronautics and Space Administration will continue to use iodine as the microbial disinfectant for potable water (PW) on manned space operations. The current method for adding iodine is the "Microbial Check Valve", a passive ion exchange device whose output is temperature dependent and also adds excess iodide to the water. An "active" electrochemical technique, using silver and inert electrodes, is proposed to allow controlled addition and removal of the iodine from the PW by cycling a silver iodide layer. The units can be physically recycled between the two locations for these modes.

The design is based upon the constrains set by the PW system, including conductivity, expected flow rates, and iodine treatment levels. The units require a minimum electrode area of 300 cm² and fits into a space of 3x3x5 cm. The efficiency of iodine and iodide removal will depend upon the thickness of silver iodide on the silver electrode, which under nominal conditions could approach 40 μ m in 90 days of operation. The time between recycling the units will also depend upon the iodine removal efficiency.

The equilibria for iodine species in the water were evaluated. Graphs for the iodine species, carbonate species and hydrogen ion are presented, based upon levels of iodine added and total inorganic carbon present. The effect of temperature on the residual level of iodine (iodide) and silver in the water is graphically presented. The oxidation and reduction reactions were also examined at the expected concentrations of reactive species in the PW to test the feasibility of the iodine removal and generation processes. The major difficulty encountered was due to the presents of oxygen in the water. While oxygen could possibly help in removing excess iodide, it would cause a problem in the controlled generation of iodine due to its preferential reduction relative to that of silver iodide.

The analytical chemistry required to monitor the performance of the PW system was reviewed. It is clear that potentiometric measurements (like pH) are inaccurate in pure water, but it is possible for conductivity techniques with ion selective electrodes can make accurate measurements. Methods based upon conductivity were used to calculate pH and the concentrations of iodine species in treated water. These methods allowed a check upon the accuracy of the total trace ion analysis of the PW. The report makes a final point that oxygen should be routinely monitored in the PW system.

INTRODUCTION

The National Aeronautics and Space Administration (NASA) plans on using iodine for microbial control in the recycled Iodine is potable water (PW) system on its Space Station. currently used on the Space Transportation System (STS) missions where the water is not recycled but is obtained as a byproduct from the fuel cells. Because of its convenient method of addition and its adequate disinfectant properties, iodine will probably be used in future long duration space ventures like missions to Mars and Lunar base facilities. There is limited experience with the long term use of iodine disinfectant in water and it could present some potential health problems. These include possible formation of toxic compounds from the reaction of iodine with organic material (residual or in the stomach) and increased iodide levels effecting the thyroid function. Iodine levels some what above nominal will give water a noticeable and objectionable taste (however even pure water is noted for its objectionable "flat" taste.) Thus, it would be desireable and perhaps necessary to remove nearly all of the iodine species before the water is consumed. In some situations it may be important to recycle the iodine.

Currently NASA is adding iodine to PW systems by means of a "microbial check valve" (MCV), an effective PASSIVE DEVICE. The MCV consist of a chamber containing a anion exchange resin loaded with iodine (mainly as the triiodide ion, I3) which delivers low levels of iodine (I_2) , iodide (I^-) and hydrogen ion (H+) to the water. The behavior of iodine in this system is characterized by a set of chemical equilibria involving both the ion exchange material and reactions of water. During use the I2 level slowly drops as the resin iodine load decreasesa. The equilibrium constants for these processes are temperature dependent and high temperature water can produce iodine levels above the acceptable limits. The MCV also produces H⁺ and excess I , even when operating at normal temperatures, and the pH of the treated water can fall significantly below the pH 6 limit for the Space Station PW1. These problems could be overcome by removing the excess iodine and related ions just before the water is used.

At present NASA has no device for this end-use treatment but they are considering using a high capacity ion exchange unit, working in the reverse mode of the MCV. However the end-use position of the unit requires it to treat hot water where the chemical equilibria are not favorable. Vapor,

a. Unpublished results from Water and Food Analysis Lab, NASA, Johnson Space Center, Houston TX.

liquid or chemical extraction of ${\rm I}_2$ from the water is conceivable, but most methods appear bulky and not suitable for microgravity conditions.

As an alternative to the MCV system, I have studied the possibility of an ACTIVE electrochemical technique for generating, recycling and removing I_2 and its associated ions in PW. In this report the device will be called the EC-MCV (electrochemical microbial check valve), though based upon its construction it is often referred to as the "silver bullet". This report discusses a design based upon the limiting requirements for PW treatment in both the Space Station and STS environments. The advantages of the EC-MCV will be presented along with some possible limiting complications that need to be investigated.

OVERVIEW OF THE EC-MCV

In principle the operation of the EC-MCV is simple and can be followed on the schematic diagram in Figure 1:

- o In the Iodine Removal Mode (IRM) the silver electrode reacts spontaneously with any iodine (I₂) or other active iodine species in solution to form a very insoluble coating of silver iodide (AgI). Excess iodide (I⁻) can be removed by oxidizing the silver electrode under a controlled potential to form more AgI.
- o In the Iodine Generation Mode (IGM) a controlled current is past through the device and the AgI on the silver electrode is reduced to silver and iodide (I^-) is released into the water. Upon reaching the counter electrode the I^- is oxidized to I_2 . The iodine level in the water is controlled by the electrode current relative to the water flow rate.

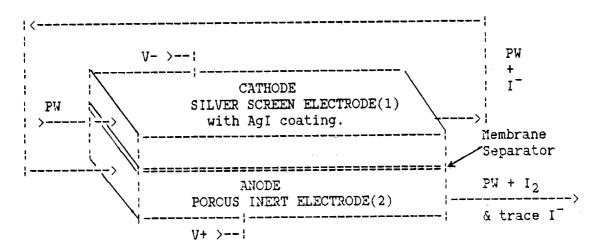
CONSTRAINTS ON THE EC-MCV DESIGN

The nature of the PW system puts severe constraints on practical designs of the EC-MCV and some basic research will be needed to prove this a viable concept.

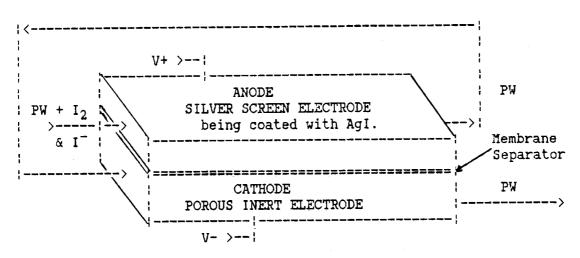
Conductivity

A major design limitation is the low conductivity of the PW, which is measured in units of Siemens/cm (S/cm) for a one cm² area. Its reciprocal (resistivity) is often used and is given in ohm cm. Completely pure water has a value of 0.056 μ S/cm or 18.3 M Ω cm. Water samples from the Biofilm Test Bed (BTB), a system designed to simulate aspects of the PW system for the Space Station, have values of 0.2 to 0.5 μ S/cm². These low values limit the current densities that the water

can carry with reasonable applied voltages. For an electric field of 1 V/cm the PW will only support current densities of 0.2 to 0.5 $\mu\text{A/cm}^2$. Water from the STS fuel cells may be more pure and have lower conductivity. For water with 2 ppm of I_2 added the conductivity increase to about 2 $\mu\text{S/cm}$.



A. Arrangement for adding I₂ to PW at a set rate by controlled current electrolysis.



B. Arrangement for removing I₂ and I from PW under controlled potential.

Figure 1.- Schematic drawing of the proposed recyclable EC-MCV.

(1) The cell consists of a stacked array of alternating thin (<1 mm) electrodes and separators. (2) Possible inert electrode materials are: platinum, titanium, tin, reticulated vitreous carbon, or carbon cloth.

Water Flow Rates

The inflow of PW is one factor determining the rate of iodine addition to the water. The anticipated Space Station flow is 25 1/day (0.3 ml/sec) of humidity condensate from the cabin. The system residence time for the treated water is expected to be about 100 hours, with most of the time in storage tanks. The demand of water at the output will be intermittent, with flows of 10 to 30 ml/sec of either hot or cold water being required^b.

Iodine Treatment Levels

Currently the planned iodine treatment level is 2 to 3 ppm, but a standard MCV using hot water from the STS fuel cells has produced levels above 10 ppm^a. For the purpose of more complete disinfection even higher levels could be allowed if the total iodine level was reduced before consumption.

Electrode Area

The above requirements set the typical rate of I_2 addition for an EC-MCV at 2 to 3 nanomol/sec, requiring a total current up to 0.6 mA. To handle this current at a current density of 0.2 μ A/cm² will require a minimum effective surface area for the electrochemical cell of 300 cm². Since the area on each side of the electrode is counted, this is equivalent to a stack of 10 pairs of 3 x 5 cm electrodes. (From here on, this report will deal with a nominal 3 ppm level of added iodine, if higher levels are under consideration the units can be scaled accordingly.)

The iodine removal mode could present some design problems if most of the added iodine ends up in the form of I and has to be removed electrochemically. At a projected flow rate of 11 ml/sec this would require a reaction rate of 26 $\mu mol/sec$ or 25 mA, which translates into a maximum electrode area of 13000 cm². This may not be a real constraint, as a EC-MCV unit should produce little or no excess I. However, the excess I output of a conventional MCV on the BTB is about 0.7 ppm² and would require a 3000 cm² surface area. The reduction of $\rm I_2$ in the system is another source of I, but these problems may be irrelevant if oxygen is present, see the section on Redox Reactions.

Electrode Construction

A practical design for the electrodes should approach 100

b. Private communication from Richard L. Sauer, PE, NASA SD4, Johnson Space Center, Houston TX.

% efficiency for the electrode reactions producing ${\rm I}_2$ from ${\rm I}^$ and forming AgI. To keep the voltage drop low and to maximize the water contact time, the water flow must parallel the electrodes while the charge migration is at right angle through a membrane separator. This requires thin (<1mm) porous electrodes that produce turbulent flow and narrow stagnant diffusion layers at the surface. The typical diffusion distance for an ion is about 40 μm in 1.6 sec and 200 μm in 60 sec^2 . Tending to counter these requirements is the need for the electrodes to have good electrical conductivity, low flow resistance and to be readily fabricated. While one electrode must be made of silver, or silver plated, the choice of material for the electrode is only limited by the need for inertness and conductivity. Finely woven metal gauzes have an adequate structure. Titanium, tantalum, or tin might be good choices and are not considered toxic metals. Platinum, palladium and gold are rather expensive and may react with iodide under oxidative potentials3. Also to be considered are flexible carbon cloth and reticulated vitreous carbon, which has an excellent pore structure but is brittle.

The calculated EC-MCV performance in Table 1 is based upon a conservative design using 15 pairs of electrodes (each pair being 2 mm thick including membrane separator) with a total area of 450 cm² in a 3x3x5 cm space. Research is needed on how the AgI film thickness effects the efficiency of the silver/iodine reaction, as this will determine how often the electrodes need to be recycled. As the silver surface is recycled it should become rough (possibly with dendritic growth) causing the surface to volume ratio to increase substantially, extending the recycle time. Now the questions are how many times can an electrode can be recycled and what limits electrode life.

TABLE 1.- EXPECTED CHANGES IN SILVER ELECTRODE WITH TIME IN THE IODINE REMOVAL MODE AT 3 PPM ${\bf I}_2$.

Time	0	7	30	90 days
Ag weight ^a	37.7	37.3	35.8	32.0 g
AgI weight	0	0.97	4.16	12.5 g
AgI thicknessb	0	3.1	13.	39 µm
Residence time ^C	1.66	1.65	1.61	1.52 sec

a. Based upon 15 layers of 3 x 5 cm electrodes of 40 mesh 10 mil smooth Ag wire gauze.

b. Calculated for a total Ag surface area of 565 cm².

c. For a 11 ml/sec flow; the IGM time is about 60 sec.

Other EC-MCV Components

The membrane separators are another critical part of the EC-MCV. They need to be thin and have high conductivity to ions, have limited water passage and be nonreactive to iodine. Nafion by Dupont, a Teflon base cation exchange resin may work well, but bipolar membranes would be preferred. The literature of battery technology may show how this problem was solved some time ago.

The best material for cell body construction is also an open question. Plastic materials like polypropylene, Teflon, epoxy, polycarbonate, and polymethylmethacrylate come to mind. The body design should allow for simple construction and repair. Some potential problems to investigate are: the degree of I_2 adsorption by the body material, is it a reservoir for active iodine, and does it limit bacterial growth on the cell body?

The electronic control for the EC-MCV will not be covered here as the circuits are very simply implemented at these low currents and modest voltages.

CONSTRAINTS ON WATER CHEMISTRY

While source water for the PW system may be fairly pure, its trace constituents and temperature can affect the function of the EC-MCV (as well as the MCV) and the I_2 water chemistry.

Fuel Cell Water

STS fuel cell water entering the MCV is quite warm. The water should be very pure except for the possibility of entrainment of small amounts of potassium hydroxide electrolyte and residual hydrogen gas. However no excessive amounts of K⁺ or OH⁻ have shown up in analyses of PW from this source^a. It should contain no oxygen or carbon dioxide. Information on its pH and conductivity would be desirable. This water source would be a prime candidate for the EC-MCV because the regular MCV has problems treating hot water.

Humidity Condensate

The Space Station will use humidity condensate from the cabin atmosphere as its source of potable water. This source will have low levels of a number of inorganic ions and a large variety of organic chemicals, mostly in trace amounts⁴. The water should be saturated with O_2 , N_2 and CO_2 at their partial cabin pressures. After polishing the water with deionizing resins and activated charcoal filters the water should be at ambient temperature and its composition similar to that observed in the Biofilm Test Bed studies^a.

Chemical Reactions and Equilibria

The addition of I_2 to water sets up several equilibria that are sensitive to the existing pH and the I^- level. These are given in Table 2 along with several other important reactions.

TABLE 2.- CHEMICAL EQUILIBRIA NEEDED TO UNDERSTAND THE CHEMISTRY OF I2 IN WATER^{5,6}.

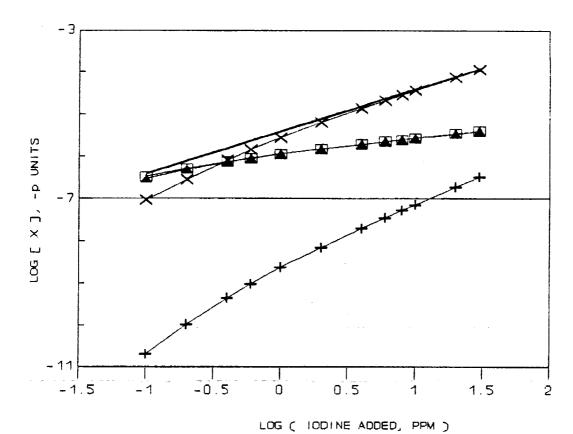
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Keq at 25 °C
              Reaction
   I_2aq + H_2O ----> HOI + I^- + H^+
                                         5.40E-13
   I_{2}^{2} ----> I_{2}^{2} + I_{2}^{2} I_{2}^{2} + I_{2}^{2}
                                         1.38E-03
                                         1.20E-11
           A\overline{g}I \longrightarrow A\overline{g}^+ + I^-
                                         8.51E-17
   N/Aa
5
                                          N/A
           H_{2}^{-}O \longrightarrow H^{+} + OH^{-}
                                         1.00E-14
    N/A
9
                                         4.30E-7
                                         5.60E-11
      These constants are not available, the ones with ResI
  represent the ion exchange equilibria of the MCV resin.
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Reactions 2 and 3 are not important as the concentrations of I_3^- and H_2OI^+ are normally insignificant in PW. However, reaction 1 produces HOI, H^+ , and I^- in amounts sufficient to give PW a 5.75 pH and provide equivalent amounts of I^- and HOI. Figure 2 shows the relationship of these species to the amount of I_2 added to pure water. If the incoming water is much above pH 7 it can divert a large portion of I_2 to HOI and I^- . In pure water the amount of dissolved CO_2 will determine the pH by reactions 8 and 9, Table 2 and Figure 3. However, in treated water the usual levels of CO_2 are 100 fold below that of I_2 and the H_2CO_3/HCO_3- ratio is controlled by the I_2 reactions.

Excess I

If I is present in the water in concentrations greater than available from the above reactions, the solution is considered to have "excess I". A major portion of the I in water treated with the regular MCV is "excess I", released from the resin by ion exchange reaction 7, Table 2. It is accompanied by equivalent amounts of H $^+$, which lowers the pH to about 5.3. Other sources of excess I are reactions which reduce I $_2$ to I and usually produce H $^+$ at the same time.

Two reactions that may be important in the PW systems are: 1) Microbial reduction of I_2 by iodine resistant bacteria, (perhaps they are using it as an energy source?). 2) The oxidation of reactive chromium or other atoms of stainless



steel in the PW system. This reaction, if it occurs, must be slow at room temperature, but possibly becomes important at higher temperatures. However no unusual amounts of Cr are seen in I_2 treated water, even though Fe, Ni, and Cr have been observed in untreated water in the BTB^a. This might imply that an I_2 oxidation could be part of a metal passivation process leading to thicker oxide coatings, but also producing more H^+ and I^- .

Silver Iodide

The formation and stability of silver iodide (AgI) plays a key role in the operation of the EC-MCV for removal of iodine species. As mentioned earlier, the effect of the AgI thickness on the rate $\rm I_2$ reacts with the underlying silver needs investigation, for the thickness can approach 40 μm in 90 days. Also important is the durability of the surface, as flaking of the AgI would interfere with recycling electrodes and could contaminate the PW. Finally, the increased solubility of the AgI with temperature may be important as the output water will often be heated prior to iodine removal.

However, Figure 4 shows that even at 100 C the Ag is still below the 50 ppb limit.

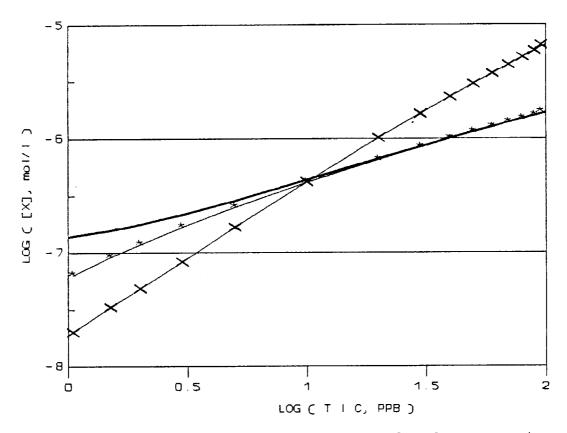


Figure 3.- Concentration of chemical species in pure water from dissolved CO_2 (reported as TIC). Legend: ---- H^+ ; --*-- HCO_3^- ; --x-- H_2CO_3 .

Redox Reactions and Electrode Potentials

Reduction and oxidation chemistry is at the heart of the generation and removal of I_2 by the EC-MCV and the significant reaction are given in Table 3. A negative cell potential indicates an electrolysis reaction controlled by an applied current or voltage. The more positive a value is the more "spontaneous" the reaction.

Included in the table are several reactions involving oxygen that may be important to the EC-MCV operation. In the iodine removal mode, without oxygen, the values for reactions 2 and 4 show that Ag reacts very vigorously with I_2 , while it requires electrolysis condition with a voltage greater than 0.31 volts to remove I^- . Note, while Ag has only the slightest tendency to react with O_2 alone, in the presence of I^- it has a very positive potential to form AgI! This could solve all the problems of "excess I^- " removal without

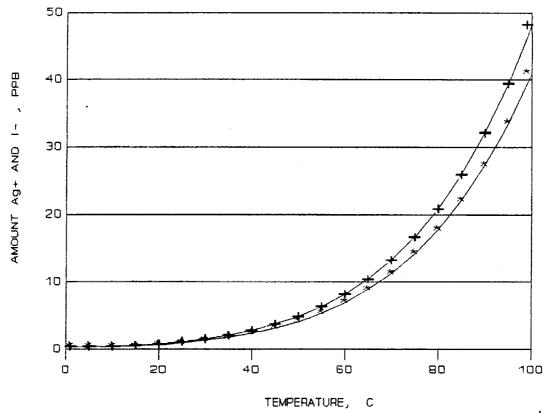


Figure 4.- The effect of temperature on the amounts of Ag^{\dagger} and I^{-} released by silver iodide surfaces. Legend: --*-- Ag^{\dagger} ; --+-- I^{-} .

electrolysis, just add oxygen. BUT, this idea must be tested experimentally, for ${\rm O}_2$ reactions are notorious for having very slow kinetics even when the thermodynamics are very favorable. On the other hand, silver and iodine reactions have catalytic activity, so hopefully the reaction will proceed. Reaction 5 also indicates that oxygen in solution would be helpful in reforming ${\rm I}_2$ from ${\rm I}^-$, but this reaction is known to be slow unless catalyzed by near ultraviolet light.

Oxygen Problem

In the iodine addition mode, reactions 6 and 7 indicate that the controlled current generation of I_2 occurs before O_2 and the process may require less than 1 volt applied to the cell. However, reaction 8 presents another problem, any oxygen dissolved in the input water will be reduced very easily and the applied current will not reduce AgI to Ag and I until all the oxygen is reduced. Thus, for the EC-MCV to work as planned, the source of water must be free of oxygen, like that from the STS fuel cells. However, in this situation oxygen is not available to help remove excess I . One

TABLE 3.- IMPORTANT OXIDATION/REDUCTION REACTION IN THE OPERATION OF THE EC-MCV. EXPECTED CELL POTENTIALS ARE LISTED FOR ANTICIPATED CONCENTRATIONS OF REACTANTS AT 25 C.

	CE	LL POTE	NTIAĻ		
IODINE REMOVAL MODE	$\mathtt{STD}^\mathtt{a}$	EXPE	CTEDD		
1 4 Ag + O_2 aq> 2 Ag ₂ O	0.102	0.060	0.006		
2 2 Ag + I_2 ag> 2 AgI		0.617			
$3 O_2 aq + 4^2 H^f + 4 Ag + 4 I^>$	1.424	0.753	0.699		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					
4 2 H ⁺ + 2 Ag + 2 I ⁻ > 2 AgI + \bar{H}_2	0.152	-0.310			
IN SOLUTION					
$5 O_2 aq + 4 H^+ + 4 I^>$	0.657	0.136	0.017		
$^{-}$ 2 1 2 2 4 2 4 2 5 2 5 2 6 2 7 2 8 2 8 2 9 2					
IODINE ADDITION MODE					
6 2 AgI $$ I_2 aq + 2 Ag	-0.767				
7 4 AgI + 2 H ₂ O $$	-1.424	-0.753	-0.699		
0_2^{2} aq + 4 H ⁺ + 4 Ag + 4 I			0.067		
$8 O_2 aq + 4 H^{+2}> O_2 aq + 4 H^+$	0.000	0.053	-0.267		
a. Reactants at unit activity, but O_2 aq and I_2 aq are					
based upon theoretical 1 molar solutions, and not saturated solutions at unit activity 7,8.					
saturated solutions at unit activity	, 0		<i>c</i>		
b. First entry for O2 saturation (1.	29 mM),	secona	ior		
10 ppb O_2 , other species: I_2 3 ppm,	рн 5.3,	and I	4.8		
$\mu \mathtt{M}$.					

solution is to electrolytically remove O_2 before iodination and afterward add it back by going thru the other half of the electrolytic cell. Another solution for the Space Station with oxygen in the water is to use the regular MCV and then remove the I_2 and excess I^- aided by the O_2 (if that reaction works) with a MCV unit filled with silver shot. This system would preclude recycling the iodine directly.

ANALYTICAL CHEMISTRY

Routine chemical and physical testing of the PW is needed to insure its quality and proper operation of the iodination system. The high purity of the PW, as typified by the BTB analyses, presents problems and challenges for analytical chemistry, especially when they will be compounded with the space environment. A review of the results the Water and Food Analysis Lab (WAFAL), NASA at Johnson Space Center, have obtained for the BTB during its year of operation are impressive^a. Using Ion Chromatography, Atomic Absorption, and Total Organic Carbon analyses they are now able to analyze for nearly all anion and cations expected in the PW, or are of concern. They have been able to get closure on the equivalents of charged ions at the ppb level and also excellent agreement with the water conductivity. However, these methods may be difficult to implement within the limitations of orbital flight and microgravity.

To monitor the performance of the iodination of PW one needs to know the total amount of iodine added, and the amounts of I_2 , I^- , CO_2 and H^+ . As found from the BTB results, the common potentiometric technique for pH is not accurate in low conductivity water^a. However, in fairly pure systems conductivity gives a very good measure of pH as the H^+ contributes 82 % to the conductivity below pH 7 and the other ions all have similar equivalent conductances⁹. Ion Selective Electrodes (ISE) in general will have the same problems as pH electrodes unless buffers are added to increase conductivity. Conductance techniques should be adaptable to ISE^{10} for ion measurements in these "pure" water systems and development of these methods should be supported.

The determination of I has been a problem for WAFAL as the photometric method depends on the H and I3 measurements, both of which where inaccurate. A technique that removes the active iodine species with metallic silver after measuring I2 photometrically is being developed to measure the residual I without interference From these data all the iodine species can be calculated accurately. It also appears feasible to carry out these same iodine measurements automatically using cathodic stripping voltammetry 11 .

Oxygen is one important component of the PW system that is not currently being measured. It should be measured at several locations in the system, as its concentrations may reflect the degree of microbial growth. The oxygen data would also be important for the proper operation of a EC-MCV and if excess oxygen or one of its reactive derivatives (ozone, superoxide or hydrogen peroxide) were injected as adjuncts for microbial control.

SUMMARY

An electrochemical method (EC-MCV) for controlling the iodine disinfectant in potable water for NASA's space operations has been proposed. The factors affecting the design and performance of the unit have been analyzed. This showed that it would be feasible to construct a recyclable unit in a small volume that will operate in either an iodine removal or addition mode. The EC-MCV should remove active iodine species rapidly from PW, but the rapid delivery rates at end-use may make complete removal of excess I difficult under some conditions. Its performance change with AgI buildup needs to be investigated, as this controls the time for recycling the unit. The EC-MCV has advantages over the passive MCV currently in use, as it would allow precise control of the I2 level and would not introduce excess I to the water. presence of oxygen in the EC-MCV needs to be investigated as it could affect the efficiency of I_2 addition and excess $I^$ removal.

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